A review of NO_x formation mechanisms in recovery furnaces

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Abstract: Review of NO_x formation studies shows that NO forms in recovery furnaces primarily by two independent mechanisms, thermal and fuel. Thermal NO formation is extremely temperature-sensitive. However, theoretical predictions indicate that recovery furnace temperatures are not high enough to form significant thermal NO. Fuel NO formation is less temperature-sensitive, and is related to fuel nitrogen content. Black liquors are shown to contain 0.05 to 0.24 weight percent fuel nitrogen. Conversion of just 20% of this would yield approximately 25-120 ppm NO_x (at 8% O_2) in the flue gas, enough to represent the majority of the total NO_x. Data from operating recovery furnaces show NO_x emissions ranging from near zero to over 100 ppm at 8% O_2. An apparent increase in recovery furnace NO_x emissions was observed with increasing solids. This increase is much less than predicted by thermal NO formation theory, indicating that other NO formation/destruction mechanisms, such as fuel NO formation. are important. No data are available to show the relative importance of thermal and fuel NO to total NO_x during black liquor combustion.

Keywords: Bibliographies, Black liquors, Combustion, Emission, Nitrogen oxides, Reaction, Mechanisms, Recovery, Furnaces.

Nitric oxide (NO) and nitrogen dioxide (NO_2) are formed during combustion whenever nitrogen is present in the fuel or in the combustion air. These oxides of nitrogen (collectively referred to as NO_x) are considered to be key constituents in reactions associated with photochemical smog and acid rain *(1)*. For protection of human health and vegetation from adverse effects, NO_x emissions from stationary combustion sources have been regulated by local and federal agencies.

Traditionally, recovery furnaces have been operated such that NO_x emission levels were below typical emission standards for coal- and residual oil-fired boilers. Surveys of NO_x emissions from kraft recovery furnaces in the late '70s *(2,3)* showed emissions in the range of 0.05-0.14 lb/million Btu (26-71 ppm on an in-stack concentration basis). At the same time, the New Source Performance Standard for large new residual oil-fired steam generators built after 1971 was 0.30 lb/million Btu.

More recently, due to improved technologies for concentrating black liquors, recovery furnaces are operating at higher levels of liquor solids concentration. Decreases in liquor moisture will result in higher combustion temperatures, and there is some concern that increased temperatures will yield increases in NO_x emissions. In several cases, observed increases in recovery furnace NO_x emissions have been related to firing higher solids concentrations *(4-8)*.

The purpose of this paper is to present basic information on the chemistry and formation of NO_x, most of which has been developed in other combustion fields (such as fossil fuel combustion), to discuss the implications for NO_x emissions from recovery furnaces, and to identify several research needs relating to the subject of recovery furnace NO_x emissions.

Mechanisms for NO_x formation

Most of the NO_x emitted by combustion sources is NO with only a small fraction (typically 5% or less) appearing as NO_2. The total NO emitted is formed by three independent mechanisms: thermal NO (the fixation of molecular nitrogen by oxygen atoms

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produced at high temperatures), fuel NO (the oxidation of nitrogen contained in the fuel during the combustion process), and prompt NO (the attack of hydrocarbon free radicals on molecular nitrogen producing NO precursors). Prompt NO is usually considered to be of minor importance for industrial furnaces *(9)*. The relative importance of each of the other two mechanisms in determining the total NO emission level is dependent on furnace temperatures and fuel nitrogen levels.

The kinetics involved in these NO formation mechanisms are generally rate limiting. Concentrations of NO measured in hot combustion gases are typically orders of magnitude less than equilibrium concentrations at hot gas temperatures. Conversely, NO levels are effectively frozen as the combustion gases are cooled, resulting in flue gas concentrations which are much greater than equilibrium concentrations at low temperatures.

Thermal NO

Thermal NO is the dominant source of NO_x emissions for combustion of fuels such as natural gas, which contain very low levels of chemically bound nitrogen. The mechanism for the formation of thermal NO was first described by Zeldovich *(10)* in 1946 as the following two reaction steps:

$$N_2 + O \leftrightarrow NO + N \quad (1)$$

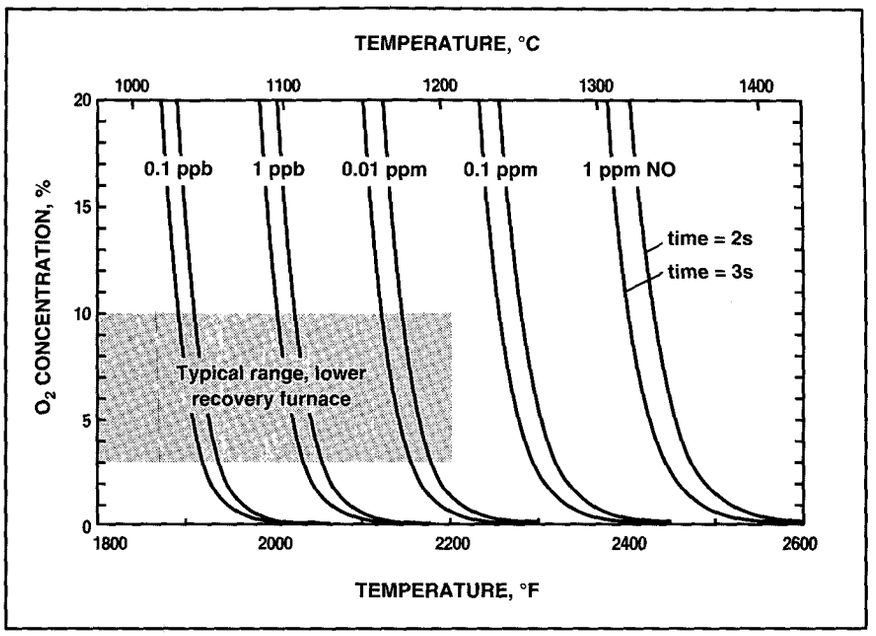
$$N + O_2 \leftrightarrow NO + O \quad (2)$$

The first step (Reaction 1) is rate-limiting and has a very high activation energy (75 kcal/gmol). This high activation energy results in high temperature sensitivity, hence the designation "thermal" NO. The Zeldovich mechanism is frequently extended *(9)* to more accurately describe thermal NO formation under fuel-rich conditions by including a third reaction step:

$$N + OH \leftrightarrow NO + H \quad (3)$$

Because thermal NO is formed to some degree during the combustion of nearly all fuels with air, this mechanism has been studied extensively.

1. Approximate temperature and oxygen dependency of thermal NO, as determined by Eq. 7

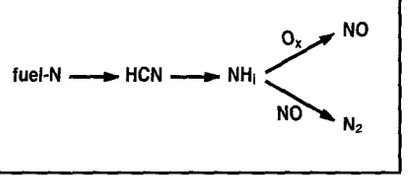


Kinetic rate coefficients for both the forward and reverse rates (of Reactions 1-3) have been reported over a wide range of temperatures *(11)*. The reactions involve primarily the oxygen-nitrogen system and can be considered, with reasonable accuracy, separately from the combustion process, since the time scale for NO formation reactions is generally greater than the time scale for combustion reactions. This fact enhances the utility of applying information derived from laboratory combustion studies on thermal NO to NO_x formation in industrial furnaces.

From the Zeldovich mechanism (Reactions 1 and 2) a simple expression can be derived to approximate the rate of thermal NO formation. In practical flames, NO concentrations are small compared to 0_2 and N_2 concentrations, and the forward rates are greater than the reverse rates. Considering only the forward reactions, and invoking the steady state assumption for atomic nitrogen (i.e., d(N)/dt=0), the following expression is obtainable for the maximum NO formation rate:

$$d(N)/dt = 2k_1(O)(N_2) \quad (4)$$

2. Overall reaction pathway for formation of NO from fuel nitrogen.



I. Nitrogen levels in 13 kraft black liquors

Mill	*Wood*	*N, % of dry solids*
1	mxd	0.05
2	swd	0.06
3	swd	0.06
4	mxd	0.06
5	swd	0.1
6	NA[a]	0.1
7	NA	0.14
8	NA	0.05
9	NA	0.14
10	NA	0.24,0.20,0.08[b]
11	NA	0.12,0.19,0.10[b]
12	NA	0.1
13	NA	0.1
Average		0.11
Standard dev.		0.06

[a] Not available
[b] Samples collected on different days

where

k_1 = rate constant for the forward rate of Reaction 1.

By assuming equilibration of the combustion reactions, the concentration of atomic oxygen can be estimated from its equilibrium with 0_2 as in Eq. 5.

$$(O) = 3.01 \cdot 10^3 \exp[-30{,}300/T] \quad (5)$$
$$(O2)^{1/2}[P/RT]^{1/2}$$

As shown by Bowman *(11)*, a generally accepted expression for the forward rate constant is Eq. 6.

$$k_1 = 1.8 \cdot 10^{11} \exp[-38{,}400/T], \quad (6)$$
$$\text{m3/kgmol/s}$$

Substitution of these expressions (Eqs. 5 and 6) into Eq. 4 yields Eq. 7:

$$d(NO)/dt = 3.79 \cdot 10^{15}/T^{1/2} \exp$$
$$[-68{,}700/T](O_2)^{1/2}\,(N_2),\ \text{kgmol/m}^3\text{/s} \quad (7)$$

where

T = gas temperature, Kelvin

t = reaction time, s

gas concentrations = $kgmol/m^3$

It is evident from this rate expression that thermal NO formation is highly temperature dependent, and is also dependent on oxygen concentration and residence time.

This is more clearly illustrated with **Fig. 1**, which is a graphical representation of Eq. 7. Figure 1 shows the potential for moderate increases in temperature to have a significant impact on thermal NO formation. Concentrations of thermal NO increase by an order of magnitude for each 100-140°F (55-80°C) increase in furnace temperature. The dependencies on oxygen concentration and residence time are less pronounced than the temperature dependency.

Considering the typical ranges of oxygen concentration and temperature in the lower recovery furnace (indicated by the shaded box in Fig. 1), it appears that the thermal NO formation mechanism is unable to account for observed recovery furnace NO_x emission levels. This prediction does not account for local temperatures, which can be much higher (by 200 ^ C or more) than average temperatures due to exothermic combustion reactors at burning particle surfaces, and due to turbulent fluctuations. Actual concentrations of oxygen atoms may exceed equilibrium. Mixing in recovery furnaces is imperfect and may lead to local oxidizing and reducing zones. Properly accounting for these factors could lead to predicted thermal NO levels in recovery furnaces which are greater than those shown in Fig. 1. In spite of these simplifying assumptions, however, it seems unlikely that temperatures in recovery furnaces are sufficiently high to result in significant thermal NO concentrations.

Figure 1 and Eq. 7 also illustrate that strategies for reducing thermal NO formation must bring about reductions in one or more of the three parameters; viz., furnace temperature, oxygen concentration, or residence time at high temperature. As discussed by Anderson and Jackson (12), demonstrated strategies for conventional steam generating boilers include biased firing, off-stoichiometric combustion (or air staging), and low excess air firing.

Fuel NO

Fuel NO is formed during combustion as a result of the oxidation of nitrogen contained in the fuel. A great deal of research has been focused on understanding the elementary steps and reaction mechanisms leading from fuel nitrogen to fuel NO. General reviews of this research are available *(13,14)*. A large number (hundreds) of reactions are involved, and many of these contain difficult-to-measure intermediates and radical species. Though an exact determination of the complete mechanism is presently not available, it is generally accepted *(11,14-16)* that the fuel NO mechanism includes a rapid (not rate limiting) conversion of fuel nitrogen compounds into intermediate nitrogen compounds (HCN, CN, NH_2, NH, N) which can either be converted to NO by attack of oxygen-containing species or be converted to N_2 by reaction with NO itself. **Figure 2** shows an overall reaction pathway which is often used to represent this process *(16)*.

Overall reaction rates of NO and N_2 formation from fuel nitrogen have been determined for laboratory hydrocarbon flames doped with simple nitrogen compounds such as ammonia, cyanogen, and pyridine *(15,16)*. These overall reaction rates measured on simpler combustion systems have also been applied with encouraging success for the prediction of fuel NO formation during coal combustion *(17)*.

Factors affecting fuel NO formation are fuel nitrogen content and concentration of oxygen in the gas. Unlike thermal NO, the formation of fuel NO is not highly sensitive to temperature changes caused by fuel heating value *(18)*. Increased fuel nitrogen content can lead to higher emissions of fuel NO, although fuel NO cannot be correlated with nitrogen content alone. The relationship between weight percent of nitrogen in fuel, and the percent of fuel nitrogen conversion to NO in practical combustors has been reported for a variety of fossil and synthetic fuels with nitrogen contents up to 2% *(1,11)*. On average, fractional conversion to NO increases with decreasing nitrogen content. The data, however, are widespread; for example, fuels containing less than 0.2% nitrogen showed conversions to NO ranging from a minimum of 20% to as high as 80%.

There are little to no data showing the fractional conversion of black liquor nitrogen to NO. Researchers investigating nitrogen dioxide pretreatment of pulp (the Prenox process) found that 5% or less of the nitrogen in nitrate added to black liquor was found as NO_x in the recovery boiler flue gases *(19)*. This may not be representative, however, since the inorganic form of

the nitrogen bound in nitrate may behave very differently from the chemical forms of nitrogen found in black liquor.

Measurements of nitrogen content for a number of kraft black liquors are shown in **Table I.** Expressed as a weight percentage of the dry liquor solids, the values are in the range of 0.05-0.24 with the average being 0.11. Using the minimum fuel nitrogen to NO conversion value of 20% discussed above, a recovery furnace burning black liquor with the range of nitrogen contents in Table I would yield NO emission levels of approximately 25-120 ppm in the flue gas at 8% O_2. This estimate suggests that fuel nitrogen is an important source of recovery furnace NO_x.

In fuel oil combustion studies *(20, 21)*, fuel NO was shown to be responsible for greater than 50% of total NO emissions during residual oil combustion at conditions of high air preheat (530°F) and about 80% of total NO without air preheat (because thermal NO was lower). The residual oil contained 0.20% nitrogen, which is within the range of black liquor nitrogen levels shown in Table I.

A question of importance to fuel NO formation is during which stage of combustion the fuel nitrogen is released (or converted) from its chemical form in the fuel to the gas phase intermediates in Fig. 2. This will affect when and where in the furnace the reaction of the intermediates will occur, and will affect the distribution of products formed (i.e., NO versus N_2). In combustion of coal, the release of fuel nitrogen occurs primarily during devolatilization, although additional nitrogen release occurs during char combustion *(22)*. Thus, the majority of the coal nitrogen is chemically bound in a manner so as to be readily volatile.

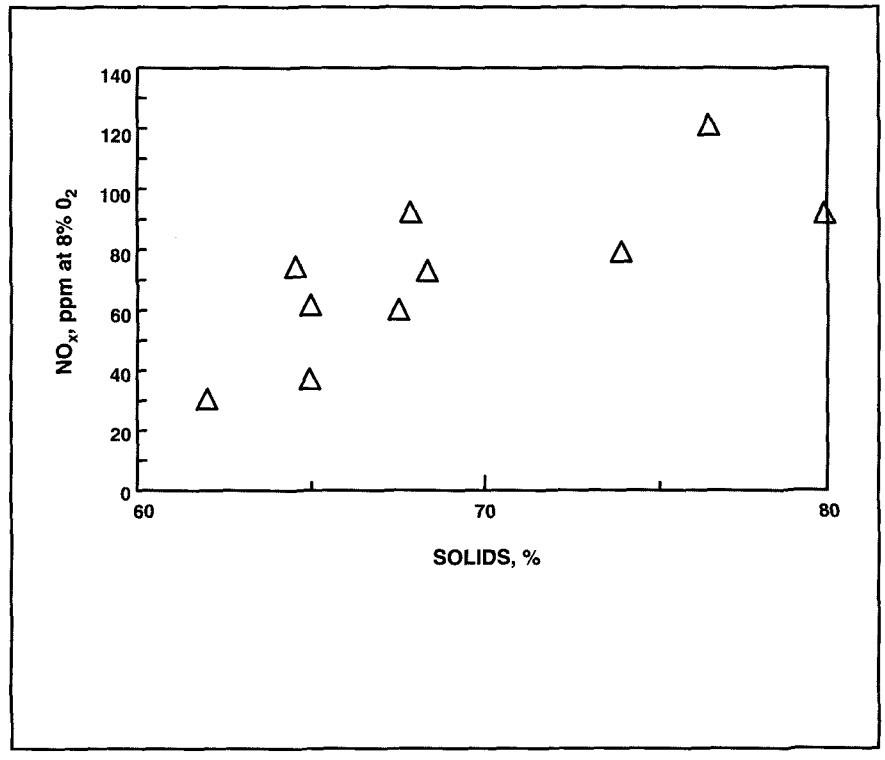
For coals, the rate at which nitrogen is released is normally slightly more rapid (by a factor of 1.2-1.5) than the rate at which carbon is burned from the fuel *(22)*. The chemical form of nitrogen in coal is thought to be

II. Summary of published NO_x flue gas concentrations from kraft and NSSC recovery furnaces

Source	*Solids, %*	*NO_x*	*NO_x, ppm at 8% O_2*
Galeano and Leopold (1971)	NA[a]	0-53 ppm	33
Galeano and Leopold (1971)[b]	NA	13-65 ppm	35
Galeano, *et al.* (1973)[b]	62	10-50 ppm	30
Hood and Miner (1981)	NA	0.05-14 lb/10^6 BTU (data from 10 furnaces)	
Bjorklund, *et al.* (1989)	64.6[d]	95 ppm	73
	76.5[d]	155 ppm	120
Brannland, *et al.* (1990)	65.0	57 mg/MJ	60
IPST data (1991)	67.6[d]	70 ppm[e]	59
IPST data (1991)	67.9[d]	110 pm[e]	91
Oscarsson, *et al.* (1991)	68	71 ppm	71
Netherton and Osborne (1991)	65	35 ppm	35
	80	90 ppm	90

[a] Not available
[b] NSSC liquor
[c] Based on approximate conversion factor of (390 ppm @ 8% O_2)/(lb/10^6 BTU).
[d] Before salt cake addition
[e] Represents average of 6 to 10 one-day tests.

3. NOx emissions observed in flue gases from recovery furnaces, effect of increasing solids. All values normalized to a common basis of 8% O2 in flue gas. Sources of data as given in Table II.



primarily heterocyclic aromatic ring structures such as pyridine, though this is difficult to ascertain because removal of the nitrogen-containing compounds from coal without their destruction is difficult. There are no data available for black liquor to show the chemical form of the fuel nitrogen, or to show how much is released during the respective stages of devolatilization and char burning.

Recovery furnace emissions

Published data on NO_x emissions from recovery furnaces are somewhat limited. **Table II** provides a summary of reported NO_x emissions along with the sources of the data *(3, 6, 8, 19, 23, 24, 25)*. Emission levels (adjusted to a common basis of ppmv at 8% O_2 in flue gas) range from near zero to over 100 ppm.

By considering those data in Table II for which liquor solids concentrations are available, a trend is apparent. These data (*plotted* in **Fig. 3**), suggest that NO_x levels increased as solids increased. A similar trend has been reported by Netherton and Osborne *(8)*. These authors reported NO_x emissions increasing monotonically from 35 ppm to 90 ppm as solids were increased from 65% to 80%. Although the data in Fig. 3 are few and are from a diversity of furnaces, a useful implication results from comparing the observed increase in NO_x emissions with increasing solids to that predicted for thermal NO formation. Theoretical flame temperature estimations for black liquor combustion *(26)* show a 230°C temperature increase for an increase in solids from 65% to 80%. Equation 7 (or Fig. 1) predicts an increase of thermal NO by a factor of several hundred for a 230°C temperature increase. Thus, the observed increase in NO_x with solids shown in Fig. 3 and reported by Netherton and Osborne (*8*) is two orders of magnitude less than predicted by thermal NO formation theory.

This difference between observation and theory implies that mechanisms other than thermal NO formation play an important role in determining recovery furnace NO_x emissions. Two possibilities are: (a) a substantial portion of the total recovery furnace NO originates as fuel NO which is not as temperature-sensitive as thermal NO, and (b) NO destruction reactions are occurring and tending to mask or partially mask the temperature dependency.

The first of these possibilities has been discussed above. The second is discussed below.

NO_x destruction reactions

Levels of NO emissions depend not only on the rate of formation of NO, but also on the rate of destruction. Once NO is formed, it can be partially destroyed before leaving the furnace. Measurements of NO profiles as a function of distance from the flame have been made in several instances *(22, 27)* in laboratory and pilot-scale combustion. Results showed that NO is rapidly formed and then slowly destroyed. Concentrations pass through a maximum in or near the flame zone and undergo reduction in the post-flame gases. The effluent or flue gas concentration does not necessarily represent the maximum level of NO concentration formed in the furnace. The reduction can be up to 50% or more of the maximum level reached in the furnace, with fuel rich flames and particle laden flames giving the most destruction, and fuel lean and homogeneous flames giving less destruction *(27, 28)*.

This NO reduction is due partially to gas-phase reaction of NO with nitrogen-containing intermediates to form N_2 (as shown in Fig. 2). The fact that the extent of NO reduction is greater in coal combustion than in gas or liquid combustion *(26)* showed that char and ash species are also responsible for NO reduction. Kinetic rates of reduction of NO to N_2 by chars have been measured *(27-29)*. Rate expressions are generally reported in the form of Eq. 8:

$$-d(\mathrm{NO})/dt = \mathrm{A}\exp[-E/(RT)]\ \mathrm{A_E}\,(\mathrm{NO}) \qquad (8)$$

showing the dependence on char external surface area (A_E), NO concentration, temperature, and residence time.

Returning to the apparent trend in Fig. 3, it is possible that NO formation in recovery furnaces increased by much more than indicated by the flue gas measurements, but that NO destruction due to air staging served to counter or dampen the increase such that only some of the increase was seen in flue gases. As discussed by Galeano and Leopold *(24)*, the conventional kraft recovery furnace, in order to promote formation of sulfide, uses the concept of air staging which is, coincidentally, a proven method for reducing NO emissions from utility boilers. Less than stoichiometric air in the lower furnace will decrease thermal NO formation by decreasing concentrations of atomic oxygen, and will decrease conversion of fuel nitrogen to NO while increasing conversion to N_2 (as shown in Fig. 2).

A destruction mechanism which may be important in recovery furnaces is the reaction of NO_x with fume species. Fume particulates represent a tremendously large surface area for reactions with gas-phase species. Sulfur gases including oxides of sulfur are known to react with fume species. It seems plausible that oxides of nitrogen may also undergo similar reducing reactions. Several possible reactions of nitrogen oxides with sodium species have been suggested *(30)* based on thermodynamic feasibility. If such reactions are occurring, burning black liquor at higher solids concentrations and higher combustion temperatures may serve to increase the fuming rate, and increases in fume-NO_x interactions would counter the increases in thermal NO formation.

Conclusions and research needs

Recovery furnace NO_x is presumed to be formed primarily by thermal and

fuel NO formation mechanisms. Little to no data are available to show the relative importance of each in black liquor combustion. This is an important question to answer and identifies a strong research need since the temperature dependence is very different for each mechanism.

Thermal NO is highly temperature-sensitive. Theory predicts that moderate increases in furnace temperature (100-140°F or 55-80°C) will yield order of magnitude increases in thermal NO concentrations. Based on theory, it appears unlikely that recovery furnace temperatures are high enough to produce significant thermal NO.

Fuel NO is much less temperature-sensitive, and thus fuel NO in recovery furnaces will not be affected by increasing solids concentrations to the same degree as will thermal NO. Black liquor solids contain 0.05-0.24 weight percent nitrogen. Conversion of 20% of this would produce NO in the range of 25-120 ppm, which is similar to the range of reported recovery furnace emissions. This suggests that fuel NO is an important source and that it may be the dominant source of recovery furnace NO emissions.

No information is available concerning the chemical form of nitrogen in black liquors, or concerning how much is released during devolatilization versus char combustion. This identifies a second research need, as this will affect when and where in the furnace the fuel nitrogen is released and will affect the relative distribution of NO and N_2 formed.

Published NO emissions data from operating recovery furnaces show values of near zero to over 100 ppm (at 8% O_2). Limited data show an increase in NO_x as solids increased from 62% to 80%. This observed increase is much less than predicted by the temperature dependence of thermal NO theory, suggesting the possibility that NO destruction reactions are occurring in recovery furnaces. This identifies a third area of research need—to evaluate the impact of potential NO_x destroying mechanisms.

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The support of the member companies and staff of the Institute of Paper Science and Technology is gratefully acknowledged. The authors give special thanks to Arun Someshwar for carefully reviewing the earlier drafts and to Terry N. Adams for providing encouragement and helpful suggestions.

Received for review Oct. 21, 1991.

Accepted March 30, 1992.